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Root Uptake and Translocation of Perfluorinated Alkyl Acids by Three Hydroponically Grown Crops

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* Supporting Information

Tomato, cabbage, and zucchini plants were grown hydroponically in a greenhouse. They were exposed to 14 perfluorinated alkyl acids (PFAAs) at four different concentrations via the nutrient solution. At maturity the plants were harvested, and the roots, stems, leaves, twigs (where applicable), and edible parts (tomatoes, cabbage head, zucchinis) were analyzed separately. Uptake and transfer factors were calculated for all plant parts to assess PFAA translocation and distribution within the plants. Root concentration factors were highest for long-chain PFAAs (>C11) in all three plant species, but these chemicals were not found in the edible parts. All other PFAAs were present in all above-ground plant parts, with transpiration stream concentration factors (TSCFs) of 0.05−0.25. These PFAAs are taken up with the transpiration stream and accumulate primarily in the leaves. Although some systematic differences were observed, overall their uptake from nutrient solution to roots and their further distribution within the plants were similar between plant species and among PFAAs.

PFAA, root uptake, translocation, crops, hydroponic, plants, PFOA, PFOS

INTRODUCTION

Perfluorinated alkyl acids (PFAAs) have been used for decades in a variety of industrial and commercial products, such as coatings for textiles and papers or firefighting foams, due to their water- and oil-repellent properties combined with their stability.[1,2] However, some of these properties also contribute to making PFAAs problematic environmental contaminants. They are not known to degrade in the environment[3] and thus can be found ubiquitously in, for instance, surface water and wildlife.[4−6] PFAAs have been detected in human blood and breast milk,[7−10] which is of concern because some PFAAs have been proven or are suspected to have adverse effects on human and animal health.[11−13] Little is known so far about how humans are exposed. Exposure risk assessment identified the human diet to be one of the major sources of PFAAs in the human body.[14−17] Although a considerable amount of data is available on PFAA concentrations in and sources of drinking water[18−20] and aquatic organisms,[21−23] little research has been done so far on crops.

Food analysis studies[16,24,25] and a screening study of vegetables in Europe by Herzke et al.[26] have shown that crops are contaminated with PFAAs, whereby concentrations in different vegetable subgroups (e.g., leafy vegetables or bulb vegetables) were observed to be similar. In a recent dietary exposure study by Klenow et al.,[27] vegetables were identified to be the most important food category for exposure to PFHxA and PFOA, with up to 69% of the total exposure coming from vegetables, depending on the location. Furthermore, studies with cattle have shown that PFAAs can be taken up by cattle from feed, thus leading to a secondary exposure pathway from contaminated crops to humans via dairy products and meat.[28,29] One possible source of PFAAs in crops is contaminated soil. Stahl et al. grew several crops (mainly cereals) in soil spiked with perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA).[30] They found a concentration-dependent uptake into plant tissues and higher concentrations in the straw of the plants than in the storage organs (e.g., tubers, ears). Roots and leaves were not analyzed in their study. Lechner and Knapp, who investigated the carry-over of PFOS and PFOA from soil to carrots, potatoes, and cucumbers, also found higher concentrations in the vegetative parts of the plant than in the storage organs.[31] They also confirmed the sorption to the potato tuber peel that Stahl et al. reported. Yoo et al. investigated the uptake of PFAAs in grass growing on soil that had been amended with biosolids containing PFAAs and found an exponential decrease of grass/soil accumulation factors with increasing carbon chain length.[32] Two other soil-related studies have been published by Stahl et al.[33] and Wen et al.[34] Both studies focus on cereals. Stahl et al. investigated the leaching of the compounds in their lysimeter study over 5 years with repeated growing of cereal plants. However, no transfer factors (TFs) and no data on soil properties were presented in their study. Wen et al. grew wheat on biosolid-amended fields and calculated TFs. They found the highest TFs for the roots for all compounds and decreasing TFs with increasing carbon chain length. In a previous study we investigated the root uptake and translocation of PFAAs to foliage in hydroponically grown lettuce.[35] PFAAs were retained mostly in the roots, with the exception of the short-chain compounds. Root/nutrient solution concentration factors were highest for the long-chain

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PFAAs, whereas foliage/root concentration factors were lowest, and it was concluded that sorption to root surface tissue was the major uptake mechanism for the long-chain PFAAs. Recently some more mechanistic uptake studies have been published, investigating the influence of abiotic parameters, such as pH values or temperature,[36,37] and investigating the influence of metabolic inhibitors on the uptake.[38] These studies have been conducted with maize and wheat plants. Although these studies provide some initial insights into plant uptake of PFAAs from soil, there is still limited mechanistic understanding of the uptake, how it is influenced by the properties of the PFAAs and the characteristics of the plants, and how the PFAAs are distributed between different plant tissues.

The goal of the present study was to investigate the uptake of PFAAs and their distribution in different plant parts. To that end three crops were grown hydroponically in a greenhouse. A hydroponic system was used so that the water uptake could be readily monitored and the bioavailable concentrations of the PFAAs in the root zone could be directly measured. Further advantages are the controlled supply of nutrients, which together with the controlled light conditions ensures an optimal growth. A limitation of hydroponic studies is that they do not include the effect of soil on modulating chemical availability. A further drawback is that the nutrient solution has to be renewed regularly, which can lead to variability in exposure concentration for surface active chemicals such as PFAAs.

The crops were chosen to represent a variety of physiology. Tomato is a fruit-bearing crop of economic importance. Zucchini is another fruit-bearing crop belonging to the family of Cucurbitaceae, which has been shown to have a unique capability to transfer some hydrophobic organic contaminants from roots to shoots.[39,40] Cabbage is an important crop of which part of the leaves (the cabbage head) is eaten, and leaves were hypothesized to be a plant tissue that would amass high concentrations of short-chain PFAAs. A set of 11 perfluorinated carboxylic acids (PFCAs; carbon chain length from C4 to C14) and 3 perfluorinated alkyl sulfonates (PFSAs; C4, C6, and C8) was selected to provide a broad foundation for assessing the influence of chemical properties on PFAA uptake and distribution. When harvested, the plants were divided into roots, stems, leaves, and edible parts (tomatoes, zucchinis, and cabbage heads) to explore PFAA distribution within the plant. In tomato and zucchini, the stem tissue was further divided into the main stem (called "stem") and the tissue connecting the main stem to the leaves ("twigs") to provide more spatial resolution in the study to the transport of the PFAAs from the roots to the above-ground plant parts.

MATERIALS AND METHODS

Chemical Reagents and Laboratory Materials. All chemicals used in this study were of the highest quality and purity available. The abbreviations, suppliers, and purities of the chemicals can be found in Table S1 of the Supporting Information (SI).

Materials used for extraction and cleanup of the samples included Florisil SPE cartridges (1000 mg, 6 mL) from Applied Separations (Allentown, PA, USA), Oasis WAX 3 cm^3 SPE cartridges (60 mg) from Waters (Wexford, Ireland), and Supelclean ENVI-Carb 120/140 from Supelco (Bellefonte, PA, USA). Polypropylene (PP) tubes (50 and 15 mL) with screw caps were purchased from Sarstedt (Numbrecht, Germany); PP vials (2.0 and 0.3 mL) were purchased from VWR International (Amsterdam, The Netherlands). Acrodisc LC13 GHP Pall 0.2 μm filters were obtained from Pall Corp. (Port Washington, NY, USA). The 10 L PP buckets were acquired from Harcotom (Purmerend, The Netherlands).

Plant Culture and Exposure Experiments. The uptake study was performed in a greenhouse (14 h of light). The plants were pregrown in soil until the seed leaves (cotyledons) were fully developed (BBCH stage 10). The soil was carefully washed off before the plants were transferred to the hydroponic system, where only the roots of the plants were exposed to the nutrient solution. The system is described in more detail in our previous study.[35] Tomato (Solanum lycopersicum var. Moneymaker) plants were grown in hydroponic solutions with nominal concentrations of 10, 100, 1000 and 10000 ng/L for each PFAA. Because the highest spiked concentration for tomatoes resulted in very high concentrations in plant parts, the zucchini (Cucurbita pepo var. Black Beauty) and cabbage (Brassica oleracea convar. capitata var. alba) plants were exposed to 10, 100, 500, and 1000 ng/L. For each plant a 10 L bucket was filled with 8 L of Hoaglands nutrient solution (see Table S2 in the SI for composition) and spiked with 100 μL/L of the respective PFAA stock solution. Six replicates per concentration were used for cabbage and tomato, whereas only four replicates could be used for zucchini due to their size. Two plants of each species were grown in unspiked nutrient solution as blank controls, and two pots without plants were used for evaporation measurements.

The plants were randomly distributed in the greenhouse room, and plant growth and water uptake were determined by weighing. The zucchini and tomato plants eventually grew too big to be moved, so no new randomization of the plant distribution was possible from then on. Furthermore, the tomato plants grew too big to be supported by the available equipment and had to be cut back from time to time. Secondary shoots were continuously removed as well. Thus, for tomato only the lower plant parts were analyzed. Pruning of tomato side shoots is a common practice and was done as soon as the secondary shoots were noticeable. The trimming of the top part of the plants was necessary and done for all plants at the same height, so that individual differences between plants were minimized. In total, the cutoff biomass for each plant was much less than the total biomass of the plants at the end of the experiment. We do not expect that the pruning and trimming had an influence on the uptake of PFAAs.

During the experiment the nutrient solution needed to be renewed several times due to the water uptake of the plants. This was done by replacing the buckets with new buckets containing freshly prepared spiked nutrient solution. Differences between the uptake of water and the uptake of PFAAs meant that the PFAA concentrations changed somewhat during the experiment. With decreasing water levels in the buckets, the PFAA concentrations in the solutions can significantly increase. We describe below how we dealt with these complications. On average, the tomato plants took up 46.7 L of the nutrient solution, the cabbage plants 24.6 L, and the zucchini plants 41.4 L.

Tomato and zucchini fruits were harvested when they were ripe. Other plant parts were collected for analysis only after the experiment was stopped. Cabbage plants were divided into roots, stem, leaves, and head. Tomato and zucchini plants were divided into roots, stem, twigs, leaves, and fruits. Table S3 in the SI lists start and end dates of the growth experiment as well as dates of renewal of the nutrient solution and harvest dates of tomato and zucchini fruits. Samples were stored at −20 °C until extraction. No differences in plant growth were observed between the different spiking levels, and there were no visible effects of the compounds on the plant health (discoloring, spots). Not all of the cabbages survived until the end of the experiment, but at least three plants of each concentration survived. In total, 7 of 26 cabbage plants were lost. Cabbage survival was independent of the spiked concentration, and fatalities were most likely caused by the temperature in the greenhouse. The optimal temperature range for cabbage is between 15 and 20 °C. Temperatures above 25 °C, which were experienced for several days during the cabbage growth phase, can lead to inhibited growth and dropping of the outer leaves, which was observed for all cabbage plants in the experiment.

Extraction. After the plant samples had been washed with demineralized water, the material was dried superficially and homogenized with a household blender (Braun Multiquick MX

2050). The extraction method used is based on the method of Vestergren et al.,[41] which is a modification of the method published by Hansen et al.[42] Briefly, 10 g of the homogenate was weighed in a 50 mL PP tube and spiked with mass-labeled surrogate standards. After 5 mL of 0.4 M NaOH solution was added and vortex-mixed, the samples were left in the refrigerator overnight to allow the internal standards to distribute in the plant matrix. Next, 4 mL of 0.5 M TBA solution and 5 mL of a carbonate buffer (0.25 M Na_2CO_3/$NaHCO_3$) were added to the samples and thoroughly mixed. After the addition of 10 mL of MTBE and vortex-mixing for 1 min, the samples were sonicated for 10 min. Phase separation was achieved by centrifuging for 10 min at 3000 rpm. The MTBE phase was transferred to a new 50 mL PP tube and the extraction repeated two times. The extracts were combined and concentrated to approximately 2 mL using a Rapidvap (Labconco Corp., Kansas City, MO, USA). Florisil SPE-cartridges were prepared with 1 g sodium sulfate on top and conditioned with 10 mL MeOH and 10 mL MTBE before they were loaded with the extract. The elution of the nonpolar matrix was done with 10 mL of MTBE before the target compounds were washed off the cartridge with 10 mL of MeOH/MTBE (30:70, v/v). This extract was again evaporated with the Rapidvap to 1 mL final volume. An additional cleanup step following the Powley method with ENVI-Carb was added when the final extract was still strongly colored.[43]

Nutrient solution samples were extracted with Oasis WAX-SPE cartridges, except the samples from the 10 μg/L variant for tomato, which were directly injected. Between 20 and 150 mL of sample, depending on the nominal concentration, were spiked with internal standards and passed through the cartridges, which had been conditioned with 2 mL of 0.1% NH_4OH in MeOH (v/v) and 3 mL of H_2O. The loading speed was set to not exceed 2 drops per second. After the loaded cartridges had been washed with MeOH/H_2O (40:60, v/v), they were dried under vacuum before the PFAAs were eluted two times with 500 μL of 2% NH_4OH in MeOH (v/v).

All final extracts were passed through an Acrodisc LC 13 GHP Pall nylon filter into 2 mL PP vials and stored at 4 °C until analysis.

Analysis. The analysis was performed on an HPLC system (LC-20AD XR pump, SIL-20A autosampler, and SCL-10A VP system controller, Shimadzu, Kyoto, Japan) coupled with a tandem mass spectrometer (4000 QTrap, Applied Biosystems, Toronto, Canada). The HPLC was equipped with a precolumn (Pathfinder 300 PS-C_{18} column; i.d., 4.6 mm; length, 50 mm; particle diameter, 3 μm; Shimadzu, Duisburg, Germany) prior to the injection valve to remove potential background contamination. An ACE 3 C18-300 column (i.d., 2.1 mm; length, 150 mm; particle diameter, 3 μm; Advanced Chromatography Technologies, Aberdeen, Scotland) was used for separation and maintained at 30 °C. The mass spectrometer was equipped with an electrospray ionization interface, operating in the negative ionization mode, and was run in the scheduled MRM mode.

The purified extracts were diluted 1:1 with H_2O prior to analysis to match the initial composition of the mobile phase of the HPLC. A volume of 20 μL was injected. The mobile phase consisted of two eluents, A (40:60 MeOH/H_2O, v/v) and B (95:5 MeOH/H_2O; v/v; both with 2 mM ammonium acetate). The gradient used for separation and the mass transitions as well as other mass spectrometer settings can be found in the Supporting Information. Raw data were processed with Analyst software 1.5 (Applied Biosystems).

Quality Assurance and Control. Repeated extraction of a sample showed that the standard deviation of the concentrations between extractions was <10% for all analytes (n = 5, see Table S5 in the SI). Consequently, the samples were extracted once and injected in duplicate.

The concentrations were quantified using a 12-point calibration with fitted correlation lines that had an R^2 value of >0.99 for all analytes (no weighting was applied).

Our laboratory also participated successfully in various interlaboratory studies (see, e.g., ref 44). For further information on quality assurance and quality control measures, see also our previous study.[35]

In this study the average recovery of the internal standards was between 48% (PFBA) and 97% (PFDoA). Recoveries were determined by comparison with matrix extracts spiked with mass-labeled standards prior to injection. Interestingly, some matrices affected the signal of the compounds quite intensively. Cabbage head and zucchini roots, for example, reduced the PFBA signal by up to 80%. Signal enhancement on the other hand was at most 12%. See Tables S6 and S7 in the Supporting Information for detailed information on recoveries and matrix effects for all compounds and all matrices.

Limits of quantification (LoQs) (Table S8 in the SI) were calculated on the basis of the lowest validated calibration standard (signal to noise ratio ≥ 10). The LoQ was derived from the analyte mass injected scaled up to an extract volume of 1 mL and divided by the average extracted sample quantity for the matrix. Method blanks were prepared repeatedly with the same extraction procedure as the samples, but showed no quantifiable contamination. Solvent blanks were injected every 10 injections to check for contamination from the LC system and for memory effects, but no contamination or memory effects were observed.

Background concentrations were taken from plants growing in nonspiked nutrient solution (n = 2) and used to correct the PFAA concentrations found in spiked experiments by subtraction. Any resulting concentrations below the LoQ were neglected.

The nonbranched (further referred to as "linear PFOS (L-PFOS)") and branched isomers of PFOS were quantified separately, assuming equal response factors for branched and nonbranched isomers. Branched isomers for other PFAAs were also observed but were not quantified.

Data Analysis. Uptake factors calculated from the data were evaluated for outliers using box plots with SigmaPlot (Systat Software, Inc., Chicago, IL. USA). Outliers and values below the LoQ were not included in data interpretation. Statistical analysis of the data was performed using IBM SPSS 21 (IBM, Armonk, NY, USA). One-way analysis of variance (ANOVA) in combination with the Tukey test was conducted to assess the significance of differences between spiking levels and plant species. t tests were performed to evaluate the differences between compounds. All statements regarding differences in this study are based on a significance level of $p < 0.05$.

RESULTS AND DISCUSSION

Because there is no evidence for microbial, physical, or any other degradation of PFAAs, we consider the breakdown of the PFAAs to have been negligible in all matrices analyzed.

PFAA Concentrations in Nutrient Solution. With increasing water uptake the nutrient solution in the hydroponic system was depleted. When there was only a small volume left, high PFAA concentrations were measured that frequently exceeded the nominal spiked concentrations. There are two possible explanations. (I) As described in our previous study[35] and also shown by Reth et al.,[45] PFAAs accumulate at the air−water interface. This has been observed to be particularly pronounced for long-chain PFAAs. When only a small volume of water was left in the bucket, it was not possible to avoid sampling some surface water. This would have led to sampling of PFAAs that had accumulated at the water−air interface, which may have resulted in elevated concentrations in the sample. (II) The plants may take up water more efficiently than they take up PFAAs. This would have resulted in an enrichment of the compounds in the water and thus higher concentrations with time.

For the tomato, zucchini, and cabbage plants, the nutrient solution volumes at the time of sampling went down to a minimum of 113 mL. To calculate uptake factors, we determined average PFAA concentrations in the bulk solution that the plants had been exposed to during the entire period of exposure. To interpolate the concentrations in time and between pots, the following equations were used to calculate the nominal and bulk PFAA concentrations for each day:

$$C_{nom(t)} = \frac{(C_{nom(t-1)} \times V_{(t-1)}) - ((V_{(t-1)} - V_{(t)} - V_{evap}) \times f \times C_{bulk(t-1)}}{V_{(t)}} \quad (1)$$

$$C_{bulk(t)} = \frac{C_{nom(t)} \times V_{(t)}}{V_{(t)} + K \times A \times 1000000} \quad (2)$$

f is the effectiveness of the plant's uptake of the PFAA with the nutrient solution, K is the interface to bulk solution partition coefficient (m), V is the volume of nutrient solution (m^3), and A is the area of the air/nutrient solution interface in the bucket (m^2). The average bulk concentrations in the spike control pots were used as the initial values of C_{bulk} and (together with the nominal concentrations and A) to calculate K. For each PFAA and plant species, f was then fitted against the amount of PFAA taken up by the plant (i.e., f was chosen such that the median quotient of the predicted and measured mass of the PFAA in the plant was equal to 1). For tomato, where the total amount of PFAA taken up was not measured, we estimated the total amount by using the concentrations for the lower plant parts also for the mid and top plant parts. The resulting values for f for tomato were similar to the ones for cabbage and zucchini. The water concentrations calculated for the sampling days were quite close to the measured water concentrations. The daily concentrations estimated in this manner were used to calculate average bulk concentrations weighted with the water volume transpired by the plants. These bulk concentrations were employed to calculate plant tissue concentration factors (see below).

Roots. The PFAA uptake in the roots was assessed using the root concentration factor (RCF). The RCF was defined as the ratio between the concentration of a compound in roots and its bulk concentration in the nutrient solution to which the roots were exposed:[46]

$$RCF = \frac{\text{concn in root (ng/g FW)}}{\text{concn in nutrient solution (ng/mL)}} \quad (3)$$

Over a broad concentration range, a linear relationship between exposure concentration and uptake of PFAAs was observed by Stahl et al.[30] and in our previous study.[35] We therefore averaged the RCFs from the different exposure concentrations. If the ANOVA−Tukey test showed that the RCF from a given exposure concentration was significantly different from all other exposure concentrations, then this value was excluded from the calculation of the mean RCF. For tomato, PFDoA, PFTrA, and PFTeA had significantly lower RCFs at the highest spiking level tested (10000 ng/L). This was not observed for cabbage and zucchini, which may be due to the lower maximum spiking level tested (1000 ng/L). We also observed lower RCF values for long-chain PFCAs (especially PFDoA, PFTrA, and PFTeA) in the 10000 ng/L spiking level in our lettuce study, where we concluded that the nonlinear uptake was caused by the nonlinear adsorption of the compounds to the root surface.[35] For cabbage the lowest spiking concentration resulted in significantly higher RCFs for PFOA, PFNA, PFDA, and Br-PFOS than for the other spiking concentrations. For zucchini the RCF for PFDA was significantly higher for the lowest spiking level than for other spiking levels. We have no explanation for these observations.

The RCFs for the PFCAs generally increased markedly with increasing chain length between PFBA and PFUnA and were quite similar for PFUnA through PFTeA (Figure 1). The RCFs for the PFSAs generally increased with increasing chain length

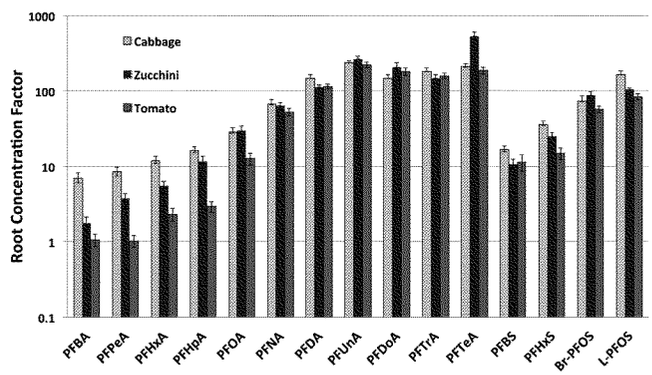

Figure 1. Root concentration factors (RCFs) for cabbage, zucchini, and tomato [(ng g^{-1})/(ng mL^{-1})]. The mean RCFs from each spiking level were averaged, whereby outliers were excluded (see text). Note the logarithmic scale. The error bars denote the standard error.

for all species. Different measures of hydrophobicity also increase with increasing chain length (SI Table S14), suggesting that the magnitude of root uptake may be determined by the hydrophobicity of the PFAA. However, for PFCAs with C > 11 the RCFs do not increase further, and hydrophobicity factors are not available for PFTrA and PFTeA, so it cannot be said with certainty that the root uptake is related to the hydrophobicity alone. The relationship between RCF and PFAA chain length is very similar to the relationship observed for lettuce in our previous study. The most pronounced difference is that lettuce showed a minimum RCF for PFHxA, whereas the three species studied here did not.

For the lettuce study we discussed two mechanisms for root uptake: sorption to the tissue between the root surface and the Casparian strip and uptake across the Casparian strip into vascular root tissue. We concluded that for lettuce sorption to root surface tissue is the dominant process for root uptake of the long-chain PFCAs, whereas for the short-chain PFCAs and PFSAs uptake across the Casparian strip into the vascular root tissue might be equally or more relevant.[35] Further support for this explanation can be found in the results presented below, which show that the stem concentration factors (SCFs) of PFDA are more than an order of magnitude less than the RCFs, even though PFDA has leaf concentration factors that are comparable to the short-chain PFCAs. Should uptake across the Casparian strip into vascular root tissue be the primary root uptake mechanism, one would expect the RCF and SCF to be similar if the vascular tissue in the roots and stem had similar sorption capacities for PFDA. The fact that the SCF is much smaller suggests that the sorption capacity of the root vascular tissue must be much greater than the sorption capacity of the stem vascular tissue or that sorption to the tissue between the root surface and the Casparian strip is an important root uptake mechanism for PFDA.

Above-ground Plant Parts. The distribution of PFAAs in the plant was assessed using various concentration factors. Concentration factors for each plant part (stem, leaves, twigs for tomato and zucchini, and edible parts) relative to the nutrient solution were calculated in the same way as the RCF and named analogously stem concentration factor (SCF), leaf concentration factor (LCF), twig concentration factor (TCF), and edible part concentration factor (ECF). Additionally,

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concentration factors between plant parts (e.g., edible part/stem) were calculated to obtain insight into the translocation of the compounds within the plants.

Stem. All species had SCFs >1 for most of the compounds with the exceptions of PFBA, PFTrA, and PFTeA for zucchini and PFHpA, PFTrA, and PFBS for cabbage. The SCF for PFTeA for cabbage could not be calculated because the concentrations in the stem were below the LoQ (Figure 2). SCF values >1 denote an accumulation in the stem. The SCF values were in general much lower than the RCF values.

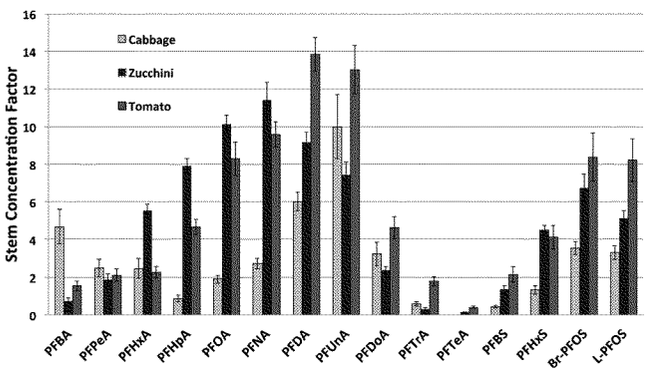

Figure 2. Stem concentration factors (SCFs) for cabbage, zucchini, and tomato [[(ng g^{-1})/(ng mL^{-1})]. The mean SCFs from each spiking level were averaged. The error bars denote the standard error.

The magnitude of the SCF is expected to depend largely on (I) the amount of PFAA being delivered by the transpiration stream from the roots and (II) the balance between retention of the PFAA in stem tissue versus further translocation with the transpiration stream to twigs and leaves. Lower SCFs were observed for the short-chain PFAAs (Figure 2). An explanation could be that the short-chain PFAAs do not partition as strongly into the stem tissue as their longer chain analogues. This could result in them not being retained in the stem tissue to the same extent, but rather being translocated further into other plant tissues. The higher SCF values of the C8−C11 PFAAs on the other hand can likely be explained by comparatively stronger sorption of the compounds on the stem tissue, resulting in stronger retention in the stem tissue and less translocation to twigs and leaves. An increase in organic matter/water partition coefficients with increasing PFAA chain length has been reported, for example, for sediment.[47] Also, experimentally determined hydrophobicity factors as well as modeled K_{OW} values have been observed to increase with increasing chain length[48,49] (SI Table S14). Therefore, it is not surprising that longer chain compounds are more retained in the stem tissue than short-chain compounds.

All three plant species showed a sharp decrease of the SCF for PFCAs with a chain length longer than C11. This is an indication that the translocation of these chemicals through the roots is considerably less efficient. One explanation could be restrictions on the ability of long-chain PFCAs to cross the Casparian strip. Another could be stronger partitioning of the long-chain PFCAs out of the xylem into the vascular tissue of the roots (see discussion under Roots above).

The low SCFs for the long-chain PFCAs also strengthen the argument for sorption to surface tissue being the dominant root uptake mechanism for these substances. Whereas the long-chain PFCAs had very low SCFs, they had the highest RCFs. Consequently, only a very small portion of the long-chain PFCAs in the roots was translocated to the stem.

Twigs. Twigs are present only in tomato and zucchini, because the leaves of cabbage grow directly on the stem. The twigs of zucchini are actually elongated leaf stalks (petioles), but because of their size they were analyzed separately from the leaf. The relationship between TCF and PFAA chain length was quite similar to the pattern observed for SCF, with the exception of PFBA and PFBS for tomato, where TCFs were much higher than SCFs (SI Figure S2). Furthermore, the twig/stem concentration factors (SI Figure S3) were close to 1 for most of the PFAAs with the notable exceptions of PFBA (3.3 in zucchini and 4.0 in tomato) and PFBS (4.0 in tomato). The explanations given for the SCFs can also be applied here.

Leaves. The LCFs were >1 in all plant species for all PFAAs except the long-chain PFCAs (Figure 3). This shows that all

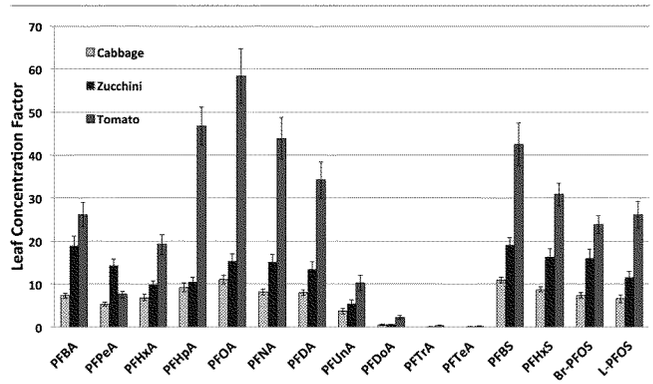

Figure 3. Leaf concentration factors (LCFs) for cabbage, zucchini, and tomato [[(ng g^{-1})/(ng mL^{-1})]. The mean LCFs from each spiking level were averaged. The error bars denote the standard error.

three plant species translocate all PFAAs except the long-chain PFCAs to the leaves and accumulate them there. One remarkable feature of these results is the similarity in the LCF values in a given plant for all compounds except the PFCAs >C10. The LCF values vary by a factor of <2 in both cabbage and zucchini. This indicates that the efficiency of these two plants at transferring the chemicals from nutrient solution to the leaves is relatively independent of the physical chemical properties within the property range bracketed by PFBA and PFDA/PFOS. Tomato shows a slightly different pattern with a maximum for PFOA and a pronounced minimum for PFPeA. The much lower LCF values for the PFCAs >C10 for all plants, despite their high RCF values (Figure 1), suggest that these substances are not transported effectively from the roots to the leaves. This was already indicated by the SCF and TCF results.

There were systematic differences in the LCFs between the plants; for zucchini and tomato they were on average 4.02 and 1.78 times higher, respectively, than for cabbage (with the exception of PFPeA in tomato). Factors that could influence the LCF include the amount of water transpired (higher transpiration would be expected to increase LCF) and leaf biomass (a high leaf biomass would tend to decrease LCF). However, no correlation could be found between LCFs and transpiration volumes, leaf biomass, or the quotient of these two parameters. The LCF is the result of more complex interactions among different plant tissues. More mechanistic insight into this is provided later.

Compared with the concentration factors of the other above-ground parts of the plants, the leaves show the highest

concentration factors for most of the compounds. The mass distributions of the chemicals between the different plant tissues show that of the above-ground tissues, the leaves also store the largest mass of all of the PFAAs (with the exception of PFPeA in tomato, Table 1 and Tables S9/S10 in the SI). This

Table 1. Mass Distribution of PFAAs in Different Tissues of Tomato Plants, Expressed as Percent of the Total Amount of PFAA Taken up by the Plant[a]

	Roots	Stem	Twig	Leaf	Fruit
PFBA	3%	4%	10%	43%	40%
PFPeA	5%	8%	7%	20%	60%
PFHxA	12%	8%	9%	42%	30%
PFHpA	12%	8%	9%	67%	4%
PFOA	29%	7%	9%	53%	1%
PFNA	56%	5%	7%	32%	0%
PFDA	72%	5%	5%	17%	0%
PFUnA	88%	4%	4%	5%	0%
PFDoA	90%	5%	3%	2%	0%
PFTrA	96%	2%	1%	1%	0%
PFTeA	98%	1%	0%	1%	0%
PFBS	21%	4%	9%	65%	1%
PFHxS	38%	5%	7%	49%	0%
Br-PFOS	68%	6%	5%	21%	0%
L-PFOS	71%	5%	4%	19%	0%

[a]Values shown are averages from all plants.

can be explained by the transpiration occurring in the leaves. The PFAAs are translocated to the leaves in the transpiration stream; there the water transpires and the PFAAs remain as residues in the leaves, where they accumulate.

Edible Part. In the edible part (i.e., cabbage head and tomato and zucchini fruits), no concentrations were detected above the LOQ for the long-chain PFCAs (C12−C14), not even at the highest tested exposure concentration (Table S11 in the SI). Consequently, no uptake factors could be calculated for these compounds.

The ECFs (Figure 4) were highest for the short-chain PFCAs and decrease with increasing chain length. Zucchini fruits were

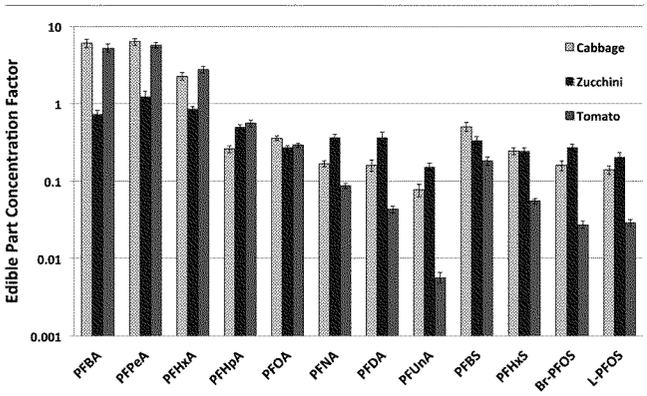

Figure 4. Edible part concentration factors (ECFs) for cabbage, zucchini, and tomato [[(ng g^{-1})/(ng mL^{-1})]. The mean ECFs from each spiking level were averaged. The error bars denote the standard error. Note the logarithmic scale.

far less contaminated than tomato fruits or cabbage heads. Thus, the exceptional ability of zucchini to accumulate some organic compounds such as polychlorinated dibenzo-p-dioxins (PCDDs) from soil[39] or water[40,50] was not observed for PFAAs.

The edible part/leaf transfer factors provide insight into the processes governing PFAA accumulation in the edible parts. Transpiration is low in fruits and in the cabbage head (which is tightly packed in leaves). The material for their development is provided by the phloem sap, which is produced in the leaves. It is thus to be expected that PFAAs will reach the fruits primarily via phloem sap. The efficiency of the leaf to fruit transfer of PFAAs can be assessed using the edible part/leaf transfer factor. All values were <1 in all cases (SI Figure S5), with values close to 1 for PFBA and PFPeA for cabbage and tomato. Because these two compounds sorb very little and transpiration is low from the edible parts, values close to 1 can be expected. The edible part/leaf transfer factor was similar for most compounds in zucchini and cabbage. For tomato it decreased exponentially with increasing chain length, and the difference between PFBA and PFUnA amounted to >3 orders of magnitude. A possible explanation for the different transport in the phloem sap is differences in the phloem sap composition, for example, different proteins.

Transpiration Stream Concentration Factor. The transpiration stream concentration factor (TSCF) describes the translocation potential of compounds from roots to aerial plant parts. Normally the TSCF is the concentration of the chemical in the transpiration stream divided by concentration in soil pore water.[46,51] Because direct measurement of the concentration in the transpiration stream was not possible, we estimated the TSCF by dividing the mass of the PFAAs in the aerial plant parts by the PFAA concentration in the nutrient solution multiplied by the volume of water transpired by the plant:

$$\text{TSCF} = [\text{concn in foliage (ng/g)} \times \text{foliage wt (g)}] / [\text{concn in nutrient solution (ng/mL)} \times \text{water transpired (mL)}] \quad (4)$$

Estimating the TSCF in this manner requires the assumptions that the compounds are not degraded in the plant, no chemical elimination from the plant occurs (e.g., loss of the compounds from the leaves to the atmosphere or back to the roots), and there is no other uptake pathway than through the roots (i.e., no atmospheric deposition). Due to the high persistence of the PFAAs and the low concentrations of the PFAAs in the above-ground parts of the control plants (no spiking with PFAAs of the nutrient solution), these assumptions are reasonable.

The TSCF values for cabbage, zucchini, and tomato thus calculated ranged between 0.05 and 0.23, with much lower values for the C12−C14 PFCAs (Figure 5). The TSCF values are relatively similar between compounds (generally a factor of <2) and between plant species (generally a factor of <2.5). There is, nevertheless, a consistent pattern in the TSCF values between the plants, with zucchini having significantly lower TSCF values than the other two tested species for all compounds except PFDoA. Because the TSCF was always <1, the transfer from the nutrient solution to the vegetative parts of the plants was inhibited. The pattern over chain length is similar for all three plant species and shows a minimum for PFHxA and a maximum for PFOA. This is also comparable to the pattern for lettuce from our previous study, with the difference that markedly higher values were measured for PFBA and the long-chain PFCAs (C > 10) in lettuce.

There is no consistent trend with the carbon chain length of the compounds, and there is no correlation between TSCF and

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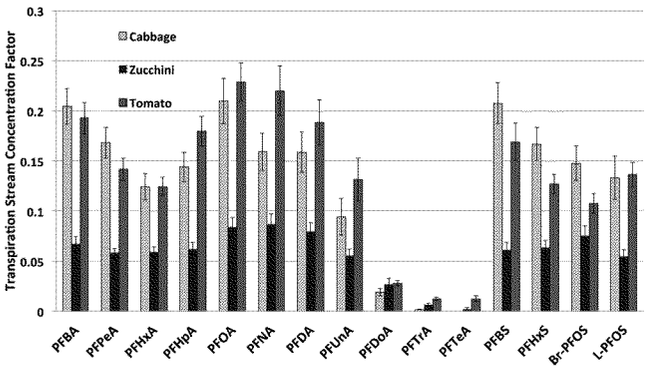

Figure 5. Transpiration stream concentration factors (TSCFs) for cabbage, zucchini, and tomato. The mean RCFs from each spiking level were averaged. The error bars denote the standard error.

measures of hydrophobicity such as log K_{OW} or log D_{OW} (SI Table S14). Briggs et al. reported that the TSCFs of nonionized chemicals depend on their log K_{OW} values and found the highest TSCF for compounds with a log K_{OW} of around 2.[51] As we discussed in our previous study,[35] PFAAs do not fit this model, as the PFAAs with a log K_{OW} around 2 show the lowest TSCF values, with the exception of the long-chain PFCAs.

Recently, Krippner et al.[37] reported a small influence of pH on the uptake of PFDA in maize roots, but found no influence of pH for C4−C9 PFCAs, PFBS, PFHxS, or PFOS. Due to very low pK_a values of PFAAs,[52] the compounds are in their ionic form at environmentally relevant pH levels. All plants in this study were grown in nutrient solutions with the same pH, so that interspecies differences cannot be explained by the influence of the pH.

Differences between Functional Groups and Isomers. To assess the influence of the PFAA functional group on PFAA uptake from soil and distribution in plants, PFBS was compared to PFPeA, PFHxS to PFHpA, and L-PFOS to PFNA, because these are pairs of compounds with the same length of perfluorinated carbon chain. Furthermore, branched and linear PFOS were compared to provide insight into the uptake of different isomers.

All PFSAs had significantly higher RCFs than the PFCAs with the same number of fluorinated carbon atoms by a factor of about 2−3. This shows that the uptake or adsorption is not only governed by the length of the fluorinated C chain, but rather by a combination of chain length and functional group. Higgins et al. came to similar conclusions when investigating the sorption of PFAAs to soils.[47] They found that the sorption of sulfonates was stronger than that of the carboxylic analogues. The higher RCFs for PFSAs correspond to higher values of several measures of hydrophobicity. The modeled log K_{OW}, as well as the experimentally determined log k_0 and log $P^{0'}$ (see Table S14 in the SI) are generally higher for the PFSAs than for their carboxylic analogues. However, this does not apply for the log D_{OW} values of the compounds.

In contrast, there were few significant differences in the TSCF between the PFSAs and the corresponding PFCAs. This suggests that the functional group had a minor influence on the uptake of the chemical into the root vascular tissue. Consequently, the stronger contribution of the sulfonate functional group to the RCF noted above is likely due to its contribution to a higher sorption to root surface tissue.

The transfer from leaves to the edible part was significantly higher for PFPeA and PFHpA than for the corresponding PFSAs. No difference was found between PFNA and L-PFOS.

A preference for the root uptake of the linear PFOS over the branched PFOS was also found for all species, but the difference was significant for only cabbage and tomato (Figure 1). This might be attributable to the smaller molecular volume of Br-PFOS resulting in lower root surface tissue/water sorption coefficients. However, no significant difference between branched and linear PFOS was found for the TSCF or the edible part/leaf concentration factor.

Clearly, some elements of the root uptake of PFAAs and their distribution in plants are influenced by the PFAA's functional group as well as its chain length.

Implications for Human Exposure. PFAA concentrations in the edible part were relatively low. The European Food Safety Authority (EFSA) has defined tolerable daily intake values (TDIs) for PFOA and PFOS of 1500 and 150 ng/kg body weight, respectively.[53] PFOA and PFOS concentrations in the edible parts of plants grown in the 1 μg/L exposure concentration did not exceed 0.5 and 0.2 ng/g fresh weight, respectively. Thus, to exceed the TDI for PFOA and PFOS, a person weighing 70 kg would need to eat around 210 and 50 kg, respectively, of these contaminated crops daily, which is of course impossible. The concentrations of the short-chain PFCAs were higher than the PFOA concentrations by up to a factor of ~23 in cabbage and tomato and a factor of ~5 in zucchini. Although no TDIs for these compounds exist, their toxicity is reported to be lower than for PFOA.[54] Because the concentrations of the most abundant PFAAs in tap and surface water are usually in the lower nanogram per liter range,[18] hydroponically grown crops generally should not be a danger to human health. However, should plants be exposed to much higher concentrations in soil or nutrient solution due to severe contamination, it is conceivable that TDI values could be exceeded and a risk for human health could occur.

All edible part/leaf transfer factors were <1 in all cases (see above and Figure S5 in the SI), which indicates that leafy crops with open leaves, such as spinach or some lettuce varieties, accumulate higher amounts in the edible part than fruit-bearing crops. Thus, leafy crops pose a higher risk for human exposure.

Mechanistic Description. The results of the present study can be summarized in the following simple mechanistic description of plant uptake of PFAAs from soil or nutrient solution and their distribution in plant tissue. PFAAs are taken up by the roots via the transpiration stream. With the exception of long-chain PFCAs (C > 10), their concentration in the transpiration stream entering the stem is ~15% of the concentration in the nutrient solution. The majority of the PFAAs that enter the stem are carried with the transpiration stream to the leaves, where the transpiration of the water results in local accumulation of PFAAs. From the leaves, all PFAAs with the exception of long-chain PFCAs (C > 11) are transported via the phloem sap to the fruit and storage organs. Less PFAA accumulates in the fruit than in the leaves, which can in part be explained by the lower transpiration rate from fruits. There are species-specific differences in the effectiveness of this transfer: In cabbage and zucchini the effectiveness is similar both across chemicals and between species, whereas in tomato there is a pronounced decrease in transfer effectiveness with increasing chain length of the PFAAs. For the roots, there is a second accumulation mechanism in addition to the uptake with the transpiration stream, namely, sorption to root surface

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tissue, which is especially important for the long-chain PFAAs. There was great consistency in this picture of PFAA uptake and distribution among the three plants studied here as well as the lettuce from the earlier study, the most notable difference being that lettuce also translocated long-chain PFCAs (C11−C14) to the above-ground plant parts.

This mechanistic description is plausible on the basis of the current understanding of contaminant behavior in plants and PFAA properties. However, it is based on controlled laboratory experiments in hydroponic solutions. Its applicability to plants growing in soil under field conditions needs to be demonstrated. The soil-related studies found in the literature do not provide enough information to calculate pore-water concentrations. Consequently, we believe that further experimental work is required to further develop our understanding of soil to plant transfer of PFAAs.

ASSOCIATED CONTENT

* Supporting Information

Additional graphics and tables as mentioned. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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